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Cross Sectional Concentration Data for Selected Organic Contaminants in River Waters near the Confluence of the Mississippi River and the Illinois, Missouri, and Ohio Rivers, June 1989 and May–June 1990

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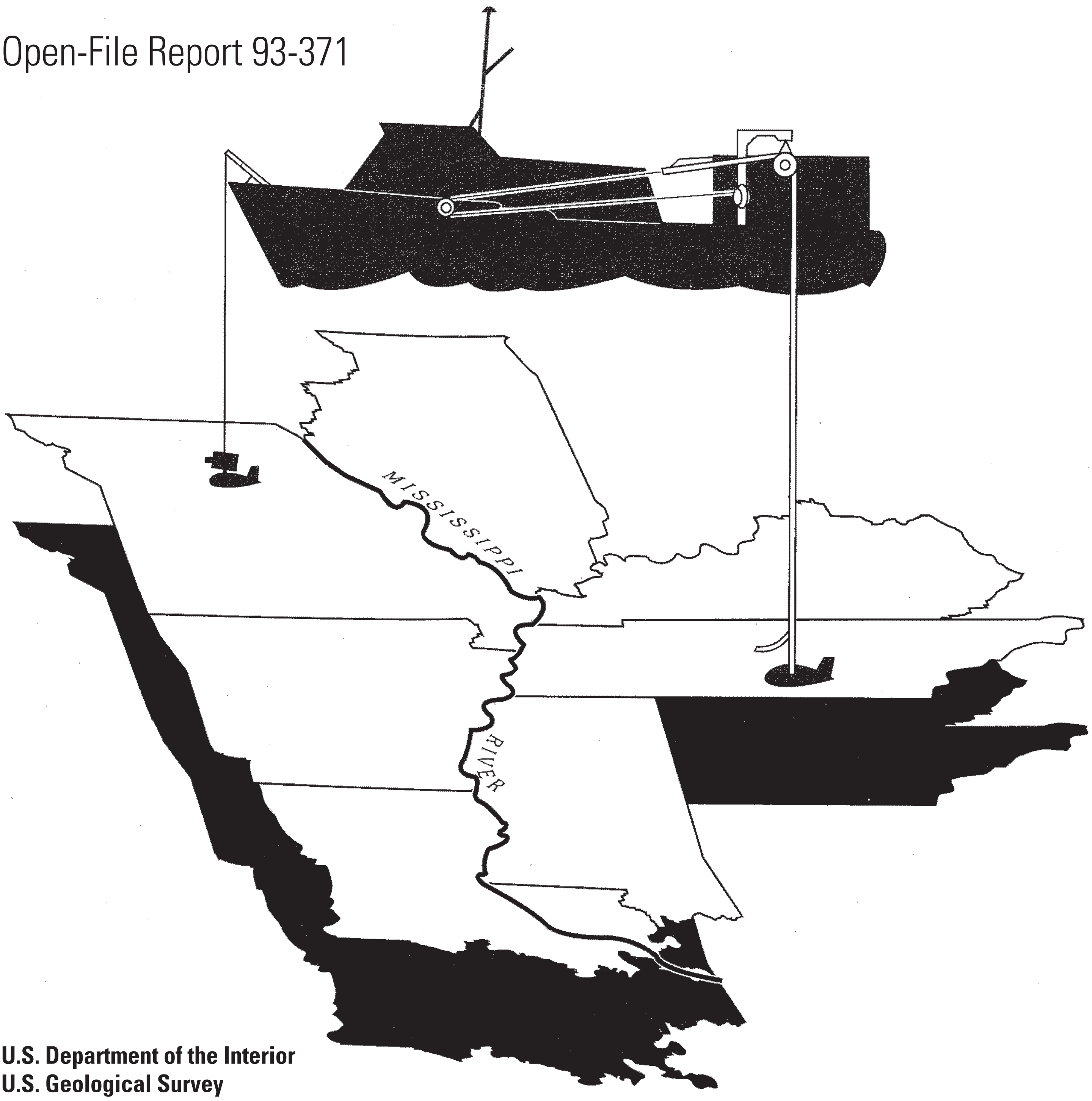

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By Colleen E. Rostad, LaDonna M. Bishop, Wilfred E. Pereira, and
Thomas J. Leiker

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Conversion Factors

Multiply	By	To obtain
	Length	
meter (m)	3.281	foot (ft)
micrometer (µm)	3.937×10^{-5}	inch (in.)
kilometer (km)	3.281	foot (ft)
	Volume	
liter (L)	0.2642	gallon (gal)
microliter (µL)	3.531×10^{-8}	cubic foot (ft^3)
milliliter (mL)	3.531×10^{-5}	cubic foot (ft^3)
	Mass	
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	ounce, avoirdupois (oz)

Cross Sectional Concentration Data for Selected Organic Contaminants in River Waters near the Confluence of the Mississippi River and the Illinois, Missouri, and Ohio Rivers, June 1989 and May-June 1990

By Colleen E. Rostad, LaDonna M. Bishop, Wilfred E. Pereira, and Thomas J. Leiker

Abstract

Water samples were collected upstream and downstream from the confluence of the Ohio River and Mississippi River to study mixing of the river waters. Samples collected in June 1989 on the Mississippi River were analyzed for alachlor, atrazine, 2-chloro-2',6'-diethylacetanilide, cyanazine, desethyl-atrazine, desisopropylatrazine, 2,6-diethylaniline, 2-hydroxy-2',6'-diethylacetanilide, metolachlor, simazine, trimethyltriazinetrione, tris(2-chloroethyl) phosphate, and tris(chloroisopropyl) phosphate. Samples collected upstream and downstream from the confluence of the Ohio River and Mississippi River in May-June 1990 were analyzed for trimethyltriazinetrione, tris(2-chloroethyl) phosphate, and tris(chloroisopropyl) phosphate. Concentration data for six to fifteen locations across the rivers are presented in tabular form for two sites in 1989 and six sites in 1990.

Introduction

A knowledge of how rivers mix at and downstream from their confluence provides a basis for prediction of pollutant transport and dilution; such information can be gained by assessment of the distribution of contaminants in the river water. The U.S. Geological Survey conducted a study of pollutant transport in the Mississippi River from St. Louis, Missouri to New Orleans, Louisiana from July 1987 to June 1990.

The sampling protocol for the Mississippi River study from July 1987 to June 1989 consisted of collecting composite samples along cross-sections of the river and selected tributaries. The sampling protocol was expanded in June 1989 to include discrete samples collected at verticals along a cross-section. Water samples were collected at two sites—one site downriver from the Upper Mississippi-Missouri-Illinois River confluence near St. Louis, Missouri, and one site downriver from the Upper Mississippi-Ohio River confluence near Hickman, Kentucky.

In May-June 1990 the study focused on the Upper Mississippi-Ohio River confluence and was expanded to seven sampling sites. The purpose of this phase of the study was to compare the transverse mixing that occurs along a straight reach of the river with the mixing that occurs along a curved reach of river. The straight reach started at the sampling site at Wickliffe, Kentucky (5 kilometers (km) downriver from the confluence), and ended 23 km downriver at the sampling site near Columbus, Kentucky. The curved reach started at the sampling site above New Madrid, Missouri (88 km downriver from the confluence), and ended 83 km downriver at the sampling site at Point Pleasant, Missouri. The Point Pleasant, Missouri, sample was lost, however. The final sampling site was at Caruthersville, Missouri (171 km downriver from the confluence), and was presumed to be a location where the Upper Mississippi and Ohio Rivers had completely mixed. Additionally, two upriver sites were sampled to determine initial concentrations of industrial organic contaminants prior to mixing: Cairo, Illinois 12 km upriver from the confluence on the Upper Mississippi River, and Olmsted, Illinois 27 km upriver from the confluence on the Ohio River. The samples collected during this phase of the study were analyzed for three industrial organic contaminants. Data in this report include results of analyses from June 1989 to July 1990.

Purpose and Scope

This report presents (1) a brief description of the methods of sample collection, preparation, and analysis, and (2) the results of analyses for the samples collected in June 1989 and May-June 1990. The compounds for which the samples were analyzed and their typical applications are listed in table 1.

Table 1. Compounds for which samples were analyzed and their applications.

Compound	Application	Reference
Herbicides		
alachlor	Herbicide used on corn and soybean crops to control annual grasses, broadleaf weeds and nutsedge	Humburg and others, 1989
atrazine	Selective herbicide used on corn and sorghum crops to control broadleaf and grassy weeds	Humburg and others, 1989
2-chloro-2',6'- diethylacetanilide	Degradation product of alachlor	Aizawa, 1982
cyanazine	Herbicide used in controlling annual grasses and broadleaf weeds for corn, grain sorghum, and cotton	Humburg and others, 1989
desethylatrazine	Degradation product of atrazine	Aizawa, 1982
desisopropylatrazine	Degradation product of atrazine	Aizawa, 1982
2,6-diethylaniline	A starting material for the manufacturing of alachlor	
2-hydroxy-2',6'- diethylacetanilide	Degradation product of alachlor	Aizawa, 1982
metolachlor	Herbicide used in controlling annual grasses, and certain broadleaf weeds on corn and cotton crops	Humburg and others, 1989
simazine	Widely used herbicide for corn crops to control broadleaf and grass weeds	Humburg and others, 1989
Industrial organic contaminants		
trimethyltriazinetrione	unknown	
tris(2-chloroethyl) phosphate	A flame retardant and plasticizer	Hawley, 1981
tris(chloroisopropyl) phosphate	A flame retardant	Hawley, 1981

Acknowledgments

This study could not have been completed without the help of the following people. Wayne Simoneaux was instrumental in holding the research vessel within about 3-5 meters of each sampling location under difficult weather conditions and boat traffic, and Wilton Delaune operated the winch for the May-June 1990 sampling. The assistance during sampling of Terry Brinton, Pat Brown, Deborah Martin, Robert Meade, John Moody, Terry Rees, James Seeley, Herbert Stevens, and Howard Taylor was appreciated.

Sample Collection, Preparation, and Analysis

Water samples were collected on the Mississippi River at St. Louis, Missouri, on June 9, 1989 and near Hickman, Kentucky, on June 13, 1989. In May-June 1990 samples were collected upriver and downriver from the confluence of the Mississippi River and Ohio River. These sites are shown in figure 1. The samples were collected in a Teflon bag sampler using a Teflon nozzle; this sampler was lowered to the river bottom and raised back to the surface at a constant rate in order to obtain a depth-integrated sample. Further details of this procedure, the exact location of sampling sites, and associated hydrologic data are described elsewhere by Moody and Meade (1993).

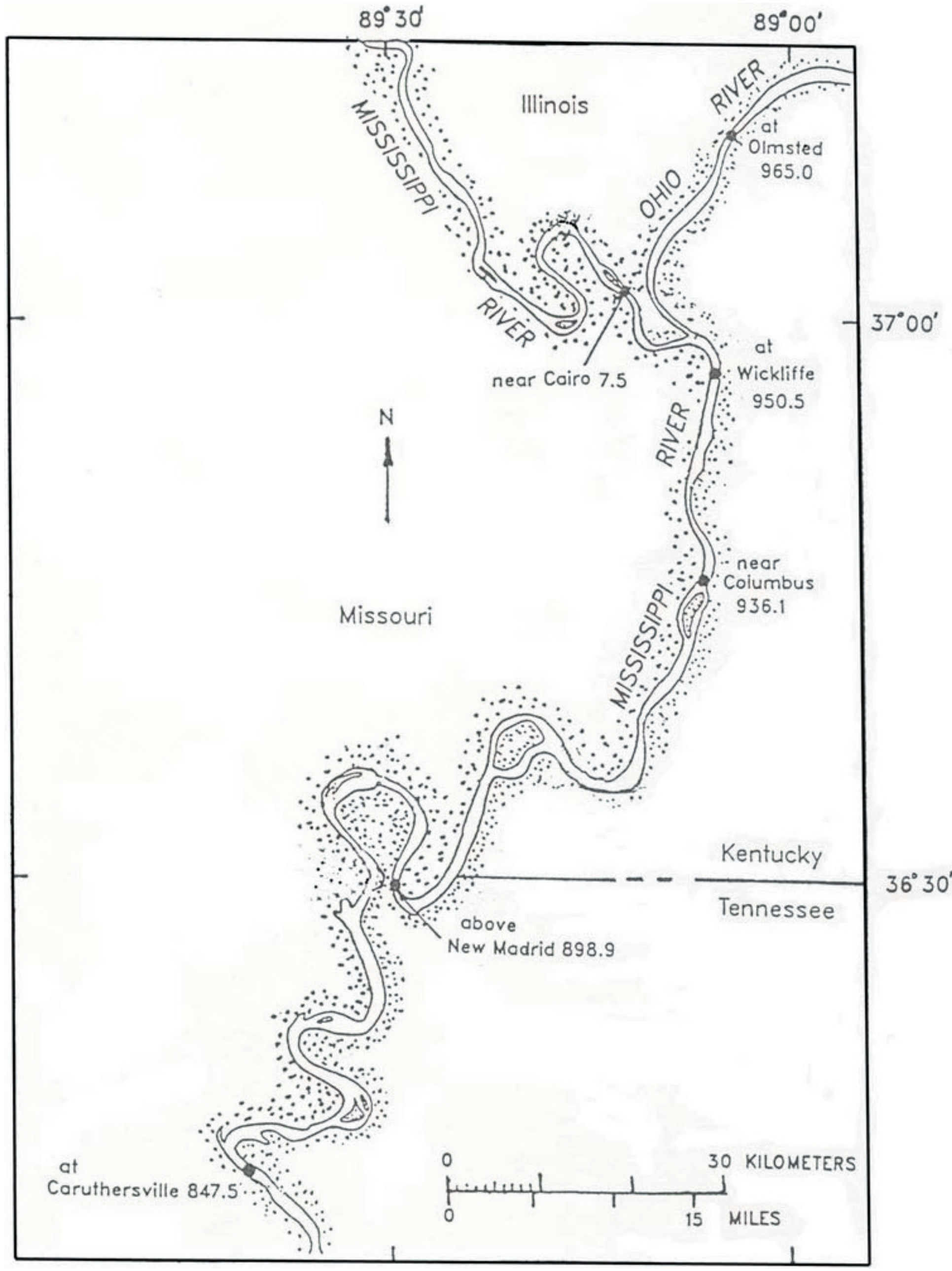

Figure 1. Location of sampling cross-sections below the confluence of the Mississippi and Ohio Rivers. The number after the site name is the river mile [modified from Moody and Meade, 1993).

A 1-liter (L) aliquot was collected for each depth-integrated sample, preserved with five drops of chloroform, and refrigerated until extraction. These samples were extracted using the following liquid-liquid extraction technique. Samples were filtered through a 0.45-micron glass-fiber filter and adjusted to pH 8.5 with 10 percent potassium hydroxide. Fifteen grams of sodium chloride and an internal standard were added to the samples, which were subsequently extracted three times with methylene chloride using 75-, 50-, and 50-mL volumes successively for the 1990 samples, and 100-, 50-, and 50-mL volumes for the 1989 samples. The combined methylene chloride extracts were dried over anhydrous sodium sulfate and concentrated in a Kuderna-Danish apparatus to an approximate volume of 5 mL. Four drops of benzene was added, and the extract was further concentrated to a volume of 100 microliters under a slow stream of dry nitrogen gas. The extracts for June 1989 and May-June 1990 samples were then analyzed for trimethyltriazinetrione, tris(2-chloroethyl)phosphate, and tris(chloroisopropyl)-phosphate by gas chromatography/positive chemical ionization/tandem mass spectrometry. The extracts for June 1989 samples were also analyzed for selected herbicides and their degradation products by using the same method (Rostad and others, 1989).

Results

The results of analyses for the June 1989 samples and the mean concentration for the replicate analyses are listed in tables 2-5. Along with the mean concentration, the uncertainty or error, which is one half the range (Taylor, 1982) in the data, is also shown. The results of analyses for the May-June 1990 samples together with the mean and uncertainty of replicate analyses are presented in tables 6-11. Note that locations from left edge of water are as viewed facing downstream.

Table 2. Herbicide data for the Mississippi River at St. Louis, Missouri, June 9, 1989. Total river width was 508 meters.

[ng/L, nanograms per liter; ±, uncertainty of duplicate analyses; nd, not detected]

	Concentration (ng/L) at points from left edge of water, in meters									
Compound	**45**	**78**	**112**	**139**	**177**	**233**	**279**	**323**	**384**	**459**
alachlor	740	720±9	730	710	660	570	520	470	600	1,600
atrazine	1,700	1390±30	1,800	1,400	1,500	1,600	1,300	1,200	1,100	1,100
2-chloro-2’,6’-diethylacetanilide	19	20±4	20	22	13	18	13	15	110	630
cyanazine	900	880±70	1,000	1,000	1,000	1,200	990	1,100	1,000	980
desethylatrazine	130	160±30	130	140	100	88	100	97	85	80
desisopropylatrazine	90	100±9	62	81	nd	21	52	nd	8.1	2.3
2,6-diethylaniline	3.5	3.4±0.2	2	2.4	2.3	1.5	1.0	4.6	90	400
2-hydroxy-2’,6’-diethylacetanilide	44	41±8	36	23	15	11	20	6.2	11	18
metolachlor	970	930±16	980	920	970	910	920	890	850	840
simazine	43.6	65±19	45	59	60	37	42	79	43	33

Table 3. Herbicide data for the Mississippi River below Hickman, Kentucky, June 13, 1989. Total river width was 1135 meters.

[ng/L, nanograms per liter; ±, uncertainty for duplicate analyses]

	Concentration (ng/L) at points from left edge of water, in meters									
Compound	**64**	**173**	**288**	**399**	**518**	**629**	**741**	**862**	**966**	**1081**
alachlor	390	430	440	420	500	560	670	650	680±20	690±10
atrazine	1,400	1,500	1,500	1,200	1,600	1,600	1,600	1,600	1300±10	1600±70
2-chloro-2’,6’-diethylacetanilide	11	8.9	11	14	20	26	49	50	49±2	54±5
cyanazine	710	780	700	670	780	850	980	900	830±80	1000±20
desethylatrazine	200	220	200	200	240	230	260	170	200±5	180±8
desisopropylatrazine	53	28	71	54	96	46	80	87	73±22	72±1
2,6-diethylaniline	0.8	1.2	1.8	2.9	7	5.8	7.5	15	13±1	13±1
2-hydroxy-2’,6’-diethylacetanilide	5.7	3.8	1.9	5.6	7.3	8.7	16	11	25±6	9.8±0.7
metolachlor	800	840	860	810	900	970	1,100	970	940±2	960±7
simazine	150	170	170	170	210	170	190	110	120±3	98±10

Table 4. Industrial organic-contaminant data for the Mississippi River at St. Louis, Missouri, June 9, 1989. Total river width was 508 meters.

[ng/L, nanograms per liter; ±, uncertainty for duplicate analyses; nd, not detected]

	Concentration (ng/L) at points from left edge of water, in meters									
Compound	**45**	**78**	**112**	**139**	**177**	**233**	**279**	**323**	**384**	**459**
trimethyltriazinetrione	0.7	1.2±0.1	nd	0.9	nd	nd	nd	1.4	0	0.5
tris(2-chloroethyl)phosphate	120	96±23	110	97	90	69	67	45	31	19
tris(chloroisopropyl)phosphate	890	820±130	790	720	660	430	340	280	160	39

Table 5. Industrial organic-contaminant data for the Mississippi River below Hickman, Kentucky, June 13, 1989. Total river width was 1,135 meters.

[ng/L, nanograms per liter; ±, uncertainty for duplicate analyses]

	Concentration (ng/L) at points from left edge of water, in meters									
Compound	**64**	**173**	**288**	**399**	**518**	**629**	**741**	**862**	**966**	**1081**
trimethyltriazinetrione	60	54	58	65	86	65	46	31	18±0	0.7
tris(2-chloroethyl)phosphate	14	13	15	18	29	32	48	52	56±0.6	59±2
tris(chloroisopropyl)phosphate	40	53	72	65	93	140	250	270	470±140	300±7

Table 6. Industrial organic-contaminant data for the Mississippi River near Cairo, Illinois, May 31, 1990. Total river width is 696 meters.

[ng/L, nanograms per liter; ±, uncertainty for duplicate analyses]

	Concentration (ng/L) at points from left edge of water, in meters					
Compound	**161**	**280**	**418**	**464**	**509**	**614**
trimethyltriazinetrione	0.4±0.3	0.8±0.6	0.7±0.5	1.7±1.1	3.2±4.5	2.5±1.9
tris(2-chloroethyl)phosphate	93±13	85±7	93±17	98±15	70±23	110±8
tris(chloroisopropyl)phosphate	98±18	88±14	94±18	97±17	89±6	110±18

Table 7. Industrial organic-contaminant data for the Mississippi River for the Ohio River at Olmsted, Illinois, May 31, 1990. Total river width was 1098 meters.

[ng/L, nanograms per liter;±, uncertainty for triplicate analyses]

	Concentration (ng/L) at points from left edge of water, in meters														
Compound	**74**	**141**	**199**	**248**	**347**	**416**	**491**	**553**	**612**	**685**	**758**	**821**	**879**	**941**	**1005**
trimethyltriazinetrione	37±5	39±6	38±5	47±5	25±5	35±5	41±11	60±13	44±8	28±7	40±9	39±6	53±7	34±7	30±12
tris(2-chloroethyl)phosphate	38±53	52±1	22±9	21±8	18±7	23±6	25±5	20±8	23±5	20±8	24±2	24±8	26±6	20±1	27±9
tris(chloroisopropyl)phosphate	19±6	41±3	23±4	29±3	19±3	24±2	21±3	21±5	22±4	22±1	22±9	34±4	25±1	20±4	21±5

Table 8. Industrial organic-contaminant data for the Mississippi River at Wickliffe, Kentucky, June 1, 1990. Total river width was 827 meters.

[ng/L, nanograms per liter; ±, uncertainty for triplicate analyses]

	Concentration (ng/L) at points from left edge of water, in meters														
Compound	**65**	**103**	**159**	**199**	**264**	**306**	**349**	**412**	**459**	**501**	**552**	**603**	**645**	**697**	**750**
trimethyl-triazinetrione	55±12	44±9	40±7	36±6	21±5	0.2±0	8.9±3.3	4.6±2.3	0.6±0.3	0.8±0.5	0.8±0.5	0.3±0.2	1.5±1.1	0.5±0.3	0.6±0.3
tris(2-chloroethyl) phosphate	22±8	31±12	28±2	34±3	71±9	53±11	86±9	99±9	170±14	96±6	110±10	110±8	99±30	99±10	110±13
tris(chloroisopropyl) phosphate	27±8	29±7	31±5	29±5	68±16	55±10	83±15	97±13	170±19	97±12	110±16	120±12	120±9	120±18	110±31

Table 9. Industrial organic-contaminant data for the Mississippi River near Columbus, Kentucky, June 1, 1990. Total river width was 912 meters.

[ng/L, nanograms per liter; ±, uncertainty for triplicate analyses]

	Concentration (ng/L) at points from left edge of water, in meters														
Compound	**69**	**118**	**170**	**229**	**283**	**336**	**412**	**461**	**507**	**581**	**630**	**680**	**725**	**784**	**851**
trimethyl-triazinetrione	47±10	37±7	36±5	27±4	13±1	8.9±1.5	5.7±0.9	3.6±0.6	4.4±0.9	1.9±0.1	3±0.5	2.4±0.1	3.2±0.2	2.6±0.4	2.8±0
tris(2-chloroethyl) phosphate	200±16	55±8	68±9	140±11	84±6	94±5	104±6	94±4.2	100±4	100±12	110±12	110±9	100±3	120±14	100±6
tris(chloroisopropyl) phosphate	52±8	35±9	42±8	78±1	72±11	83±7	100±11	84±13	100±9	95±14	110±14	110±12	100±8	120±15	97±6

Table 10. Industrial organic-contaminant data for the Mississippi River above New Madrid, Missouri, June 2, 1990. Total river width was 1,060 meters.

[ng/L, nanograms per liter; ±, uncertainty for triplicate analyses]

Compound	Concentration (ng/L) at points from left edge of water, in meters									
	120	**228**	**326**	**371**	**426**	**536**	**640**	**748**	**850**	**959**
trimethyl-triazinetrione	28±5	28±0.7	20±0.1	23±3	17±0.4	13±0.6	12.8±1	7±2	13±0.1	13±1.1
tris(2-chloroethyl) phosphate	100±9	100±12	97±15	80±12	100±13	100±10	93±1.9	95±4.2	120±5	140±5
tris(chloroisopropyl) phosphate	83±12.8	79±0.4	81±1.4	84±17	82±2.8	100±7	97±19	99±8.4	120±27	120±19

Table 11. Industrial organic-contaminant data for the Mississippi River at Caruthersville, Missouri, June 3, 1990. Total river width was 849 meters.

[ng/L, nanograms per liter; ±, uncertainty for triplicate analyses]

Compound	Concentration (ng/L) at points from left edge of water, in meters								
	95	**179**	**257**	**344**	**432**	**518**	**589**	**655**	**738**
trimethyl-triazinetrione	28±1.6	19±1.7	23±9	14±2.5	19±19	18±3	5.5±5.4	16±4.5	16±1.2
tris(2chloroethyl) phosphate	63±3.3	59±3.4	95±9	53±7.7	81±25	61±1.3	60±6.1	68±7.6	87±6.3
tris(chloroisopropyl) phosphate	79±7.4	77±11	130±27	75±1.9	130±10	72±6.6	74±8.6	86±13	86±9.4

Variation in concentration values may result from inconsistencies in sample collection, extraction, and/or analytical (instrumentation) errors. Potential errors in the sampling procedure are described by Moody and Meade (1993). Extraction and recovery variability from the liquid-liquid extraction method are unknown unless duplicate samples were extracted for analysis, which were unavailable due to sample limitations. Analytical variation was determined as the uncertainty of replicate analyses. Average, minimum, and maximum values of the uncertainty expressed as a percentage of the mean concentration for replicate analyses are presented in tables 12-13. In table 13, the large uncertainty of some values is due to instrumental variability for the polar compound, trimethyltriazinetrione, which chromatographs poorly. Average values shown in tables 12-13 were determined from non-rounded values from previous tables.

Table 12. Average, minimum, and maximum uncertainties of replicate analyses as a percentage of the mean concentration for the herbicide data.

[n.d., not determined because of insufficient data]

Compound	Average	Minimum	Maximum
Mississippi River at St. Louis, Missouri, June 9, 1989			
alachlor	1.2	n.d.	n.d.
atrazine	2.2	n.d.	n.d.
2-chloro-2’,6’-diethylacetanilide	18	n.d.	n.d.
cyanazine	8.5	n.d.	n.d.
desethylatrazine	19	n.d.	n.d.
desisopropylatrazine	8.8	n.d	n.d
2,6-diethylaniline	5.9	n.d	n.d.
2-hydroxy-2’,6’-diethylacetanilide	20	n.d.	n.d.
metolachlor	1.7	n.d.	n.d.
simazine	29	n.d.	n.d.
Mississippi River below Hickman, Kentucky, June 13, 1989			
alachlor	2.6	2.2	2.9
atrazine	2.6	0.8	4.4
2-chloro-2’,6’-diethylacetanilide	6.7	4.7	8.7
cyanazine	5.5	1.9	9.1
desethylatrazine	3.5	2.6	4.5
desisopropylatrazine	16	1.5	29
2,6-diethylaniline	4.2	3.7	4.8
2-hydroxy-2’,6’-diethylacetanilide	15	7.1	23
metolachlor	0.5	0.2	0.7
simazine	6.3	2.6	10

Table 13. Average, minimum, and maximum uncertainties for replicate analyses as a percentage of the mean concentration for the industrial organic-contaminant data.

[n.d., not determined because of insufficient data]

Compound	Average	Minimum	Maximum
Mississippi River at St. Louis, Missouri, June 9, 1989			
trimethyltriazinetrione	8.3	n.d.	n.d.
tris(2-chloroethyl) phosphate	24	n.d.	n.d.
tris(chloroisopropyl) phosphate	16	n.d.	n.d.
Mississippi River below Hickman, Kentucky, June 13, 1989			
trimethyltriazinetrione	1.8	0	3.5
tris(2-chloroethyl) phosphate	2.1	1.1	3.1
tris(chloroisopropyl) phosphate	16	2.3	29
Mississippi River near Cairo, Illinois, May 31, 1990			
trimethyltriazinetrione	83	65	140
tris(2-chloroethyl) phosphate	16	7.5	32
tris(chloroisopropyl) phosphate	16	7	19
Ohio River at Olmsted, Illinois, May 31, 1990			
trimethyltriazinetrione	19	11	38
tris(2-chloroethyl) phosphate	34	2.1	140
tris(chloroisopropyl) phosphate	17	4.4	41
Mississippi River at Wickliffe, Kentucky, June 1, 1990			
trimethyltriazinetrione	40	0	73
tris(2-chloroethyl) phosphate	15	5.9	38
tris(chloroisopropyl) phosphate	17	7.6	30
Mississippi River near Columbus, Kentucky, June 1, 1990			
trimethyltriazinetrione	13	0	22
tris(2-chloroethyl) phosphate	8.1	2.9	14
tris(chloroisopropyl) phosphate	13	6	25
Mississippi River above New Madrid, Missouri, June 2, 1990			
trimethyltriazinetrione	8.8	0.5	29
tris(2-chloroethyl) phosphate	8.6	1	15
tris(chloroisopropyl) phosphate	11	0.5	22
Mississippi River at Caruthersville, Missouri, June 3, 1990			
trimethyltriazinetrione	36	5.6	100
tris(2-chloroethyl) phosphate	11	2.1	32
tris(chloroisopropyl) phosphate	11	2.5	21

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